Fig. 2. Frontal view of the pyrazine ring along the overall molecular plane.

least-squares plane. The atoms O(15) and O(16) are slightly out of this plane, -0.129 (2) and 0.114 (2) Å respectively. All bond distances and angles within the molecule compare well with those values previously reported for analogous compounds (Beurskens et al., 1984, and references therein).

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$= 19.1$ (1), $q = 26.0$ (2), $\sum = -79.7$ (2), $\delta = 85.4$ (3), $\alpha_1 = 2.9$ (2), $\alpha_2 = -82.6$ (2)°] the ring exhibits an envelope conformation, with N(14) at the flap, distorted towards a diplanar one at the C(2)—C(3) and C(4)—C(5) bonds. Interestingly, a half-chair conformation has been described for a closely related compound with no methyl group at C(3) (Apreda, Foces-Foces, Cano & García-Blanco, 1978). The orientation of the methyl group bonded to C(1) is axial (see Fig. 2).

The distortion parameters for the 'amide groups' (Winkler & Dunitz, 1971) have been calculated from the torsion angles around the N(5)—C(6) and N(14)—C(13) bonds. As expected, the deformations with respect to sp^2 hybridization are greater at the N [$\chi_N = 21.4$ (4), 20.8 (4)°] than at the C atoms [$\chi_C = -2.5$ (4), -2.4 (4)°]. The average angles around N(5) and N(14) are 118.9 (1) and 119.0 (1)°, values confirming the sp^2 hybridization.

The diazaquinone ring is nearly planar, with no atomic deviation greater than 0.033 (2) Å from its

References

APREDA, M. C., FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1978). Acta Cryst. B34, 2666–2669.
BEURSKENS, P. T., BEURSKENS, G., APREDA, M. C., FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1984). Acta Cryst. C40, 1718–1721.
BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., PARTHASARATHI, V., BRUINS SLOT, H. J. & HALTIWANGER, R. C. (1983). DIRDIF. Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands.
CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). Tetrahedron, 33, 797–802.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WINKLER, F. K. & DUNITZ, J. D. (1971). J. Mol. Biol. 59, 169–182.

Structure of the Methanol Solvate of 13-Ethyl-18,19-dinor-17α-pregn-4-en-20-yn-17β-ol (13-Ethyl-18-norlynestrenol)

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Abstract. $C_{21}H_{30}O.CH_4O$, $M_r = 330.51$, monoclinic, $P2_1$, $a = 13.179$ (1), $b = 7.554$ (1), $c = 10.371$ (1) Å, $\beta = 93.535$ (3)°, $V = 1030.54$ (8) Å³, $Z = 2$, $D_x = 1.065$ g cm⁻³, $\lambda(\text{Cu }K\alpha) = 1.5418$ Å, $\mu = 4.41$ cm⁻¹, $F(000) = 364$, room temperature, $R = 0.044$ for 1488 unique reflections with $I \geq 2.5\sigma(I)$. The crystal was twinned by pseudomerohedry with a twin fraction of 0.146 (8); hkl data with $l = 0$ were corrected for this

effect. The overall conformation is very similar to that of lynestrenol. The conformation of the ethyl group is *trans* relative to the C/D ring junction, which is the preferred conformation in 13-ethyl steroids. Methanol is donor as well as acceptor in two hydrogen bonds connecting steroid molecules related by the 2_1 axis.

Introduction. The introduction at C(13) of an ethyl substituent instead of a methyl group in Δ^4, $\Delta^{4,9}$ and $\Delta^{4,9,11}$ unsaturated 17β-hydroxy-19-nor-17α-pregn-20-yn-3-ones (Delettre, Mornon, Lepicard, Ojasoo & Raynaud, 1980) increases progestin, androgen and glucocorticoid binding. However, the affinity data did not permit any conclusion concerning the influence of the ethyl group on the estrogen binding. As the conformation of the ethyl group is of interest in studying the binding mechanisms of the sex-hormone receptors, we undertook the structure analysis of the title compound (ELYN).

Experimental. Sample obtained through the Scientific Development Group of Organon, Oss, The Netherlands. Oscillation and Weissenberg photographs determined the space group to be $P2_1$ and showed crystals, crystallized in methanol, to be twinned by pseudo-merohedry with coinciding zones for $l = 0$. Data measured on crystal of dimensions $1\cdot3 \times 0\cdot15 \times 0\cdot15$ mm, Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation; lattice parameters refined by least-squares fitting of 2θ values of 25 reflections in range $28 < 2\theta < 48°$; ω–2θ scan mode, $\Delta\omega = (0\cdot60 + 0\cdot18\tan\theta)°$, ψ azimuth chosen such that max. number of separate reflections of both individuals could be measured, according to method described by de Boer & Duisenberg (1984). 1935 independent reflections measured up to $\theta = 70°$, $\pm h$, $-k$, $+l$ (max. range 16, 9, 12), 1488 of these considered observed $[I > 2\cdot5\sigma(I)]$ and used for structure determination and refinement. Three periodically measured standard reflections ($\bar{2}11$, 111, 201) showed intensity variations less than 7%; Lp corrections, no correction for absorption. The geometrical relation $-c/(2a\cos\beta) = 6\cdot4$ indicates that zones for $l = 6$ and $l = 7$ will contain partially coinciding non-equivalent reflections. Only a minor part of these reflections could be measured separately. For reflections with $l = 0$ the overlap is almost exact and correction for twinning of the measured intensities I_{hk0} is given by (*e.g.* van Geerestein, Kanters & Duisenberg, 1983)

$$J_{hk0} = (1-\alpha)I_{hk0},$$

where J_{hk0} is the corrected intensity for an untwinned crystal with the volume of the larger twin; α is the volume fraction of the smaller twin and was experimentally found to be $0\cdot146$ (8) by averaging the 34 strongest pairs of intensities of equivalent reflections of both individuals with indices $l = 3$ and $l = 4$, where peak separation is maximal.

Structure solved with preliminary version of *SHELXS*84 (Sheldrick, 1984); best E map gave all non-H atoms including those of solvent molecule. H atoms placed on calculated positions, except both hydroxyl-group H atoms and H atom bonded to ethynyl group, which were located on difference map. In final cycles of full-matrix least-squares refinement, using *SHELX*76 (Sheldrick, 1976), 229 parameters varied, including overall scale factor, positional and individual anisotropic parameters for C and O atoms, positional parameters for H[C(21)], H[O(17)] and H[O(m)] (see Fig. 1), orientational parameters for rigid methyl group of methanol and overall thermal parameter for H atoms. Remaining H atoms included in refinement riding on their bonded atoms. For uncorrected data, refinement on F converged at $R = 0\cdot0490$ and $wR = 0\cdot0490$, where $w = 1/\sigma^2(F)$, and for data with corrected I_{hk0} intensities at $R = 0\cdot0441$ and $wR = 0\cdot0440$. Overall thermal parameter for H atoms refined to $0\cdot102$ (2) Å^2. Since only a minor improvement can be expected, it was decided not to correct the partially overlapping data for the $hk6$ and $hk7$ zones. As the twin fraction is only 15%, this correction would not alter these intensities in a substantial way. Moreover, rather large errors will result in the corrected data, because the correction is not a simple scaling but involves addition of two twin-related intensities (Jameson, 1982). $\Delta/\sigma = 0\cdot03$ (3) (av.) and $0\cdot24$ (max.) for non-H-atom parameters and $\Delta/\sigma = 0\cdot2$ (3) (av.) and $0\cdot97$ (max.) for H-atom parameters; final difference electron density within $\pm0\cdot16$ e Å^{-3}. Scattering factors from Cromer & Mann (1968) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms.

Discussion. The final atomic parameters are given in Table 1.* The conformation of the steroid molecule and the atom numbering are shown in Fig. 1. The intramolecular dimensions involving the non-hydrogen atoms are given in Table 2. The bond lengths and angles of ELYN correspond well to those observed in other lynestrenol derivatives (Griffin, Duax & Weeks, 1984). The overall conformation of ELYN is very similar to that of the parent compound lynestrenol (Rohrer, Lauffenburger, Duax & Zeelen, 1976) and of 11β-fluorolynestrenol (Rohrer, Duax & Zeelen, 1978). The Δ^4 A ring has a 1α,2β-half-chair conformation, as indicated by the $\Delta C_2[C(1)-C(2)]$ value of $9\cdot2$ (5)°. The B and C rings are in the usual chair conformation and the D ring has a 13β-envelope conformation as indicated by the pseudorotation parameters $\Delta =$

Table 1. *Positional and equivalent isotropic thermal parameters* (Å²) *for non-H atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta.$$

	x	y	z	U_{eq}
O(17)	0·0544 (2)	0·5975 (6)	0·0870 (3)	0·0677 (8)
C(1)	0·4349 (3)	0·3815 (7)	0·6627 (4)	0·077 (2)
C(2)	0·4949 (3)	0·3752 (8)	0·7930 (5)	0·090 (2)
C(3)	0·5568 (3)	0·5417 (9)	0·8128 (5)	0·103 (2)
C(4)	0·4937 (3)	0·7030 (8)	0·7831 (4)	0·077 (2)
C(5)	0·4046 (3)	0·7015 (7)	0·7173 (3)	0·060 (1)
C(6)	0·3384 (3)	0·8655 (7)	0·7037 (3)	0·070 (1)
C(7)	0·3015 (3)	0·8998 (7)	0·5627 (3)	0·064 (1)
C(8)	0·2503 (3)	0·7350 (6)	0·5039 (3)	0·052 (1)
C(9)	0·3220 (2)	0·5754 (6)	0·5134 (3)	0·051 (1)
C(10)	0·3597 (3)	0·5375 (6)	0·6544 (3)	0·056 (1)
C(11)	0·2735 (3)	0·4122 (6)	0·4467 (3)	0·056 (1)
C(12)	0·2348 (3)	0·4468 (6)	0·3055 (3)	0·053 (1)
C(13)	0·1607 (2)	0·6044 (6)	0·2980 (3)	0·049 (1)
C(14)	0·2150 (3)	0·7632*	0·3624 (3)	0·050 (1)
C(15)	0·1459 (3)	0·9209 (7)	0·3266 (4)	0·068 (2)
C(16)	0·1002 (3)	0·8762 (6)	0·1908 (4)	0·074 (2)
C(17)	0·1354 (3)	0·6842 (7)	0·1615 (3)	0·056 (1)
C(18)	0·0601 (2)	0·5606 (7)	0·3613 (4)	0·065 (1)
C(20)	0·2254 (3)	0·6877 (7)	0·0833 (3)	0·062 (1)
C(21)	0·2950 (3)	0·6891 (8)	0·0183 (4)	0·083 (2)
C(22)	0·0118 (3)	0·3794 (7)	0·3278 (4)	0·084 (2)
O(Me)	0·1151 (2)	0·2737 (6)	0·0029 (3)	0·080 (1)
C(Me)	0·1945 (4)	0·232 (1)	−0·0756 (6)	0·121 (3)

* Kept fixed during the refinement.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *for non-H atoms with e.s.d.'s in parentheses*

O(17)–C(17)	1·437 (5)	C(9)–C(11)	1·534 (6)
C(1)–C(2)	1·524 (6)	C(11)–C(12)	1·543 (5)
C(1)–C(10)	1·539 (6)	C(12)–C(13)	1·539 (6)
C(2)–C(3)	1·506 (8)	C(13)–C(14)	1·529 (5)
C(3)–C(4)	1·496 (8)	C(13)–C(17)	1·556 (5)
C(4)–C(5)	1·321 (5)	C(13)–C(18)	1·551 (4)
C(5)–C(6)	1·517 (7)	C(14)–C(15)	1·531 (5)
C(5)–C(10)	1·504 (6)	C(15)–C(16)	1·535 (6)
C(6)–C(7)	1·534 (5)	C(16)–C(17)	1·558 (7)
C(7)–C(8)	1·525 (6)	C(17)–C(20)	1·478 (5)
C(8)–C(9)	1·531 (6)	C(18)–C(22)	1·540 (7)
C(8)–C(14)	1·527 (4)	C(20)–C(21)	1·171 (5)
C(9)–C(10)	1·542 (5)	O(Me)–C(Me)	1·401 (6)

C(2)–C(1)–C(10)	111·8 (4)	C(12)–C(13)–C(14)	107·8 (3)
C(1)–C(2)–C(3)	110·0 (4)	C(12)–C(13)–C(17)	116·5 (3)
C(2)–C(3)–C(4)	111·2 (4)	C(12)–C(13)–C(18)	111·7 (4)
C(3)–C(4)–C(5)	124·3 (5)	C(14)–C(13)–C(17)	99·3 (3)
C(4)–C(5)–C(6)	121·9 (5)	C(14)–C(13)–C(18)	111·8 (3)
C(4)–C(5)–C(10)	123·0 (5)	C(17)–C(13)–C(18)	109·1 (3)
C(6)–C(5)–C(10)	115·1 (3)	C(8)–C(14)–C(13)	114·7 (2)
C(5)–C(6)–C(7)	111·9 (3)	C(8)–C(14)–C(15)	118·9 (3)
C(6)–C(7)–C(8)	110·5 (4)	C(13)–C(14)–C(15)	104·4 (3)
C(7)–C(8)–C(9)	111·1 (3)	C(14)–C(15)–C(16)	104·2 (4)
C(7)–C(8)–C(14)	111·8 (3)	C(15)–C(16)–C(17)	106·2 (3)
C(9)–C(8)–C(14)	108·8 (3)	O(17)–C(17)–C(13)	115·0 (4)
C(8)–C(9)–C(10)	111·6 (3)	O(17)–C(17)–C(16)	108·0 (3)
C(8)–C(9)–C(11)	111·4 (3)	O(17)–C(17)–C(20)	107·9 (3)
C(10)–C(9)–C(11)	112·3 (3)	C(13)–C(17)–C(16)	103·5 (3)
C(1)–C(10)–C(5)	111·8 (3)	C(13)–C(17)–C(20)	111·8 (3)
C(1)–C(10)–C(9)	111·3 (3)	C(16)–C(17)–C(20)	110·4 (4)
C(5)–C(10)–C(9)	110·7 (3)	C(13)–C(18)–C(22)	116·5 (4)
C(9)–C(11)–C(12)	113·3 (3)	C(17)–C(20)–C(21)	178·1 (4)
C(11)–C(12)–C(13)	110·5 (3)		

18·6 (5)° and $\varphi = 47·5$ (4)° (Altona, Geise & Romers, 1968). The values of these parameters for lynestrenol are 5·8 (2), 22·5 (3) and 47·0 (2)° respectively. The overall similarity is illustrated by a least-squares fit of atoms C(1) through C(18) of ELYN and lynestrenol, resulting in a mean deviation of the fitted atoms of 0·033 (4) Å; including C(20), C(21) and O(17) results in a mean deviation of 0·042 (7) Å, where O(17) has the largest deviation (0·134 Å). This difference occurs possibly because, in contrast with lynestrenol, O(17) of ELYN is involved in hydrogen bonding. The similarities of the ring conformations are also illustrated by their least-squares fits, resulting in mean deviations of the fitted atoms of 0·014 (2), 0·014 (2), 0·013 (2) and 0·017 (3) Å for the *A, B, C* and *D* rings respectively. The conformation of the angular ethyl group is approximately *trans* with respect to the C(13)–C(14) bond [torsion angle $\varphi = $ C(14)–C(13)–C(18)–C(22) $= -165·9$ (3)°] and the same conformation ($\varphi = -164·8°$) has been observed in the crystal structure of 13-ethyl-11-methylene-18-norlynestrenol (van Soest, van Dijk & Zeelen, 1980). A scan through the Cambridge Crystallographic Database on steroids (class 51) having a C(13) angular ethyl group revealed that this conformation of the ethyl group is strongly preferred. The 20 hits, including 27 crystal structures, contain only one steroid [*rac*-3-methoxy-18-methyl-estra-1,3,5(10),8,14-pentaen-17-one (Chekhlov, Ionov, Dononov & Ananchenko, 1983)] having the ethyl group in the *gauche* conformation ($\varphi = 64·5°$), whereas the mean torsion angle φ of the other structures was found to be −165 (3)°.

The molecular packing is illustrated in Fig. 2, which shows a view down **b**. The methanol solvent molecule acts as a donor and also as an acceptor in two hydrogen bonds, and connects two steroid molecules related by the 2_1 axis. Thus, a chain of hydrogen-bonded steroid and methanol molecules is formed, →O(17)→O(Me)→O[17,(−x, y−½, −z)] with O···O distances of 2·733 (6) and 2·716 (5) Å and O—H···O angles of 176 (4) and 177 (4)° respectively. There are no C···C distances less than 3·5 Å and the shortest
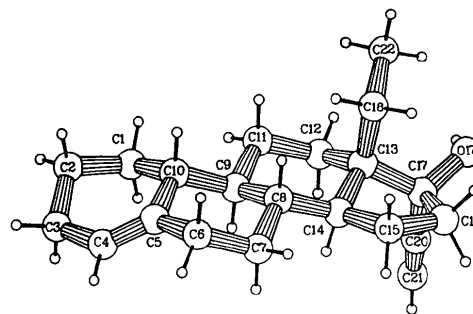

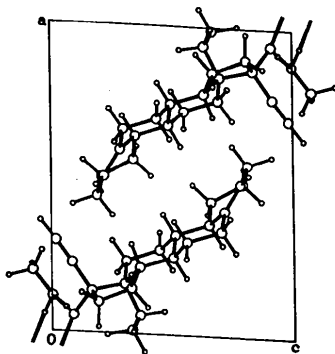Fig. 1. Molecular structure with atom numbering of 13-ethyl-18-norlynestrenol.

Fig. 2. Packing diagram viewed down b. Double lines indicate hydrogen bonds.

H···H contact is 2·185 (6) Å. The packing is different from other lynestrenol derivatives (Griffin, Duax & Weeks, 1984) and can be described as $M\ a_{36}b_{19}c_{54}\ 211$ (Duax & Norton, 1975), indicating that the molecules are packed two thick, one wide and one long, with the steroid length parallel to the ac diagonal.

We thank L. A. van Dijck of Organon for supplying the crystals.

References

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C410.

Chekhlov, A. N., Ionov, S. P., Dononov, M. V. & Ananchenko, S. N. (1983). *Bioorg. Khim.* **9**, 978.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Delettre, J., Mornon, J. P., Lepicard, G., Ojasoo, T. & Raynaud, J. P. (1980). *J. Steroid Biochem.* **13**, 45–59.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. I. New York: Ronald Press.

Geerestein, V. J. van, Kanters, J. A. & Duisenberg, A. J. M. (1983). *Acta Cryst.* **C39**, 1459–1463.

Griffin, J. F., Duax, W. L. & Weeks, C. M. (1984). *Atlas of Steroid Structure*, Vol. II. New York: Ronald Press.

Jameson, G. B. (1982). *Acta Cryst.* **A38**, 817–820.

Rohrer, D. C., Duax, W. L. & Zeelen, F. J. (1978). *Acta Cryst.* **B34**, 3801–3803.

Rohrer, D. C., Lauffenburger, J. C., Duax, W. L. & Zeelen, F. J. (1976). *Cryst. Struct. Commun.* **5**, 539–542.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1984). *SHELXS84*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Soest, T. C. van, van Dijck, L. A. & Zeelen, F. J. (1980). *Recl Trav. Chim. Pays Bas*, **99**, 323–325.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Structure of Bis(4,5,6,7,8,9-hexafluoronaphtho[2,1-b]fur-2-yl)methane

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Abstract. $C_{25}H_4F_{12}O_2$, $M_r = 564\cdot29$, monoclinic, $C2$, $a = 31\cdot86$ (3), $b = 4\cdot600$ (5), $c = 6\cdot93$ (1) Å, $\beta = 101\cdot2$ (1)°, $V = 995$ (6) Å^3, $Z = 2$, $D_m = 1\cdot90$, $D_x = 1\cdot88$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot139$ mm^{-1}, $F(000) = 556$, room temperature, $R = 0\cdot054$ for 643 observed diffractometer-measured intensities. The two halves of the molecule are related by a crystallographic twofold axis passing through the central C atom. Within each half of the molecule, the furan ring is tilted very slightly out of the plane of the naphthalene skeleton. The molecule is probably only partly delocalized, as some bonds are distinctly shorter than others.

Introduction. The compound was prepared as part of a continuing investigation into the preparation of partially fluorinated furan derivatives (Brooke & Wallis, 1982).

Its structure was determined in order to confirm the unexpected reaction product obtained when 1,3,4,-5,6,7,8-heptafluoro-2-naphthyl 2-propynyl ether was heated with 1,1,2-trichloro-1,2,2-trifluoroethane.

Experimental. Accurate cell dimensions obtained from least-squares refinement of positions of 12 strong reflections measured on a two-circle diffractometer (Mo $K\alpha$, θ_{min} 5, θ_{max} 15°, μ_{min} 0, μ_{max} 18°). Density measured by flotation and indicated $Z = 2$. 953 reflections measured on a Stoe Stadi-2 two-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation; crystal 0·04 × 0·54 × 0·19 mm, layers $k = 0$–5, $h = 0$–36, $l \pm 8$, max. $\sin\theta/\lambda = 0\cdot595$ Å^{-1}, separate standard for each layer measured every 10 reflections (intensity variation < 1%). Of the 933 unique reflections ($R_{int} = 0\cdot030$) 643 with $F > 4\sigma(F)$ used for